

# **PREDICTING ADSORPTION PROPERTIES FOR ACFs**

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## **Introduction**

Activated carbon fibers (ACFs), and activated carbon granules (ACGs) have been available for about the past 25 and 50 years, respectively. However, selection of the appropriate activated carbon to remove specific contaminants is still very much an empirical process. The problem that exists in creating a more fundamental understanding of these processes is the fact that up to now there has been no direct method for measuring the key parameters. In this paper data are presented which begin to lay the foundations for understanding the adsorption capabilities of ACFs essential to establishing a predictive model.

## **Factors that Control Adsorption in the Micropore**

Many factors control the adsorption in the micropores of the ACFs including the pore size distribution, the pore shape, the pore surface chemistry, the fiber diameter, the adsorbent form, the adsorbate size and shape, the adsorbate chemistry, the physical properties of the adsorbate, the adsorbate concentration, the adsorbate environment, and other adsorbates which may compete for similar sites. In our laboratory, many factors are being examined systematically in great detail. The present status of our work is best summarized by considering the following four questions:

- 1.) How do pores initially form in the ACFs?
- 2.) What is the structure of high surface area ACFs?
- 3.) What is the role of pore size in adsorption?
- 4.) What is the role of pore surface chemistry in adsorption?

### **How do Pores Initially Form in the ACFs?**

The origin of pore formation has recently been elucidated for ACFs (1). This discovery came about when it was observed that high surface area carbon fibers were produced during activation of phenolic fiber precursors under inert conditions. Presumably, the microporous structure was created by the evolution of volatile by-products at temperatures as low as 400-500°C and its persistence during further heating must be due to the presence of a stable crosslinked structure. Images of this microporous structure were obtained from scanning tunneling microscopy (STM) which provided direct insight into the size and shape of these initial pores. From cross-sectional images of the fiber, a remarkably homogeneous microporous structure was observed in which pores measured from several tenths of nm up to 1.1 nm in diameter with the majority of pores measuring less than 0.6 nm in diameter. At the fiber

surface, the pores were less than 5 nm in diameter and are larger than those in the bulk due to the rapid evolution of volatiles near the carbonization temperature. The initial pores which were observed from STM were not slit-shaped as originally proposed by Dubinin (2) but were ellipsoidally shaped. Thus for the first time an unambiguous interpretation now exists as to the origin of micropores in the ACFs.

### **What is the Structure of High Surface Area ACFs?**

The phenolic fibers can be further activated using an etchant or oxidizing agent. Commercially, the ACFs are activated in a mixture of CO<sub>2</sub> and steam at high temperatures (600 -800 °C) to produce a family of materials with controlled surface area ranging from 700 to 2800 m<sup>2</sup>/g (3). In practically all cases there is 2-5 % oxygen present in the ACF with a considerable percentage at the pore surface in the form of phenolic and carboxylic units.

The porous structure of the ACFs has been examined at great length using a number of indirect techniques such as fundamental adsorption theory (4), x-ray and neutron scattering (5), and adsorption of different size and shaped molecular probes (6). The greatest progress has been made with STM and we now have a database of over 800 images (7). The initial pores which were formed during carbonization begin to widen when exposed to steam/carbon dioxide due to diffusion of these etchants into the fiber bulk. Throughout activation the pores in the fiber bulk remain homogeneous and average pore sizes measure between 1 and 2 nm depending on the duration of activation (Fig. 1). Again, in contradiction to Dubinin (2), the pores remain ellipsoidally shaped in the bulk of the fiber and do not take on a slit-shaped character. Compared to the homogeneous micropores in the bulk of the fiber, the surface porosity was more heterogeneous and large mesopores and micropores were observed from the extensive reaction at the fiber surface (Fig. 2). A significant decrease in fiber diameter with increasing duration of activation was also noted where the fiber diameter decreases from 15  $\mu$ m to 9-12  $\mu$ m. The transition between the surface porosity and that in the bulk occurs in a region less than 32 nm and in this region a narrowing of the pores might lead to wedge-shaped pores.

### **What is the Role of Pore Size in Adsorption**

Pore size is one of the most important factors affecting adsorption. In order for adsorption to occur, the adsorbate must fit into the pore. Foster showed a cross-over regime for the adsorption of butane where lower surface area ACFs adsorb better at low concentrations due to a higher overlap in potential which binds the adsorbate more tightly (4). At higher concentrations the higher surface area ACFs adsorbed larger amounts due to a larger pore volume (8). From recent studies, we have observed that the cross-over regime shifts to higher concentrations with lower boiling point adsorbates and to lower concentrations with higher boiling point adsorbates (9). The APFs which have a much smaller pore size in the bulk permit enhanced adsorption of contaminants at ppm levels to ppb levels (Fig. 3). The equilibrium amount adsorbed and its dependence on adsorbate size and boiling point has been related to physical constants using fundamental adsorption theory.

The adsorption kinetics or the rate at which equilibrium adsorption is approached at a given concentration is strictly dependent on the diffusion pathlength. This property is also a function of the adsorbent size and shape, the number and size and shape of pores at the fiber surface and the number and size and shape of pores in the bulk and their

interconnectivity. Our basic studies using ACFs have shown that the rate of adsorption/desorption is faster for materials with larger pores and broader pore size distributions (Fig. 4). The larger pores facilitate fast diffusion to the smaller pores which bind the adsorbate more tightly allowing it to be adsorbed.

Therefore it becomes important to have a good distribution of large and small pores. One reason why the adsorption kinetics of the ACFs is much faster than the granules is because the ACFs have many large mesopores at the fiber surface which permits rapid access to the homogeneous microporous structure in the bulk. ACGs can not usually be tailored in this manner since they contain far fewer pores than the ACFs at their surface and typically they have a much broader pore size distribution in the bulk. One dimension for control of adsorption kinetics in ACGs is the particle diameter. Generally, as the particle diameter decreases the adsorption kinetics increase because the diffusion pathlength decreases.

As the adsorbate size decreases or the concentration decreases, materials with a larger concentration of pore sizes closer to the adsorbate size will have a higher equilibrium adsorption.

Based on these fundamental studies and others it has been possible to design/tailor adsorbents to remove contaminants from air and water to below several ppb level with little increase in estimated cost.

## **What is the Role of Pore Surface Chemistry in Adsorption**

The pore surface chemistry plays an equally critical role in adsorption and can be tailored through chemical activation or through posttreatment. The advantages of chemical activation are that a single step treatment is all that is required to control the surface chemistry and pore size and this can lead to higher reaction yields.

Activation of the phenolic precursors in air results in a high surface area fiber with acidic surface chemistry. When this fiber is activated below the carbonization temperature a unique material is formed which has higher activation yields and better wear properties (10). Under these conditions a family of adsorbents has been developed with as much as 30% oxygen in the form of phenolic hydroxyls. Based on a molecular probe study, these materials have a pore size distribution which is less than 7 Å and may be tailored by controlling the activation conditions. Through control of pore size and acidic surface chemistry, small molecules such as ammonia may be removed to low concentrations (< ppm).

Surprisingly, ammonia will etch the phenolic precursors and may be used to activate them to create high surface area carbon fibers at temperatures as low as 500°C. These materials are basic containing as much as 10 wt% nitrogen usually in the form of pyridine-like groups and aromatic amines depending on the activation conditions. Yields are much higher than that of ACFs that are posttreated in ammonia. Preliminary results have indicated that a large number of acidic contaminants can be selectively removed from air and water.

The ACFs have also been posttreated (8) in chlorine, ammonia, oxidizing agents, or hydrogen to create an ACF with a polar, basic, (basic, polar, or acidic surface chemistry depending on agent used), or neutral surface chemistry, respectively. Depending on the chemistry of the adsorbate, the ACFs can be tailored for selective removal of an adsorbate. For example, ammonia activation of a phenolic precursor permits enhanced adsorption of acidic contaminants such as HCl from air or paranitrophenol from water (Fig. 5). A post-treatment of an ACF with strong acid will produce a number of surface functionalities such as carboxylic acids, phenolic hydroxyls, and quinones. The surface of this material is therefore both acidic and polar thus enhancing the adsorption of both polar (i.e.

acetone) and basic (i.e. ammonia (11)) contaminants (Fig. 6). To date we have developed and characterized approximately 75 different materials with various surface chemistries and pore sizes (12). From these materials we have developed an extensive data base which relates the synthesis conditions to the number and type of functional groups and subsequently relates the effects of these groups to adsorption.

## Conclusions/ Future Work

Some of the key parameters important for controlling adsorption have been described in this paper. Selective adsorption of specific adsorbates has been indicated. This work provides the necessary foundation for the next step which is to establish a predictive capability. We are now in the process of relating these material features to the key engineering parameters.

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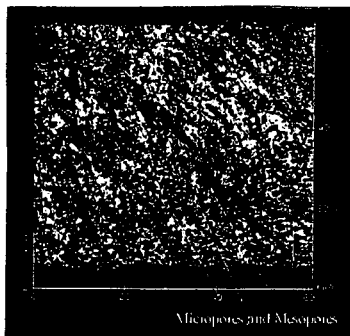


Fig. 1

STM image of the cross-section of an ACF

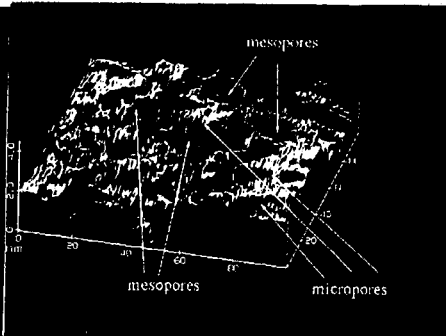


Fig. 2

STM image of the surface of an ACF

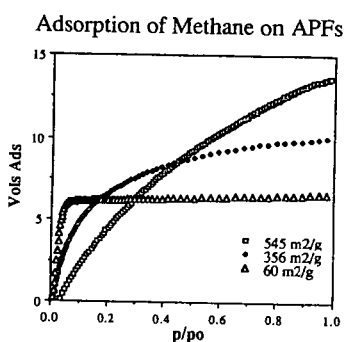


Fig. 3

Lower surface area APFs have smaller average pore sizes which adsorb larger amounts of methane at lower concentrations

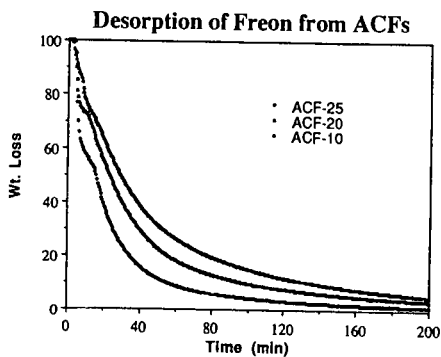


Fig. 4

The larger number ACFs have broader pore size distributions which permits for faster desorption

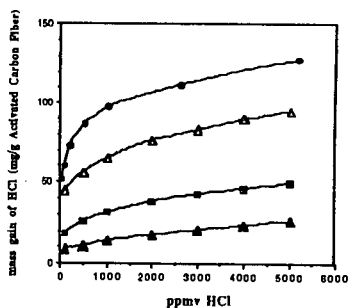


Fig. 5

As the basic character of the ACF increases (wt% N increases), the amount of HCl adsorbed increases proportionally

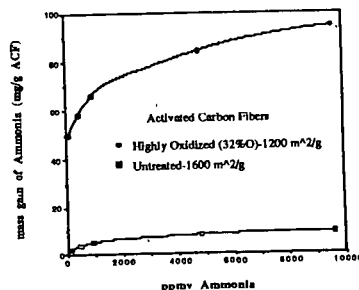


Fig. 6

As the ACF becomes more oxidized, the amount of ammonia adsorbed increases.